

FURTHER MEASUREMENTS OF THE SCINTILLATION PROPERTIES OF LEAD CARBONATE*

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ABSTRACT

Additional measurements are presented on the scintillation properties of lead carbonate (PbCO_3), a recently discovered, heavy inorganic scintillator. The light output of the natural crystal cerussite was measured during ^{60}Co irradiation at 23°C . After an exposure of $>2.5 \times 10^6$ rad the light output increased by 25% and no visible crystal coloring occurred, thus PbCO_3 appears to be useful in high radiation fields. The emission spectrum was adequately described by a sum of four gaussian peaks whose position and width did not change during the irradiation. The scintillation light output is temperature dependent, increasing with decreasing temperature from 680 photons/MeV at $+30^\circ\text{C}$ to 3200 photons/MeV at -40°C to 11,900 photons/MeV at -120°C . The scintillation decay lifetime was measured with the delayed coincidence method between $+30^\circ\text{C}$ and -140°C and fit to the sum of four exponentials. At 30°C the four components are 20% at 3.9 ns, 44% at 24 ns, 26% at 186 ns, and 11% at 1.40 μs . At -40°C the four components are 24% at 37 ns, 45% at 107 ns, 18% at 359 ns, and 12% at 1.07 μs . At -120°C the four components are 0.3% at 1.8 ns, 3.5% at 3.8 ns, 40% at 539 ns, and 56% at 2.71 μs . From 30°C to -140°C the initial flux remains constant at about 45 photons/ns/MeV. This indicates that, with decreasing temperature, the energy resolution of PbCO_3 improves, the dead time increases, and the timing resolution remains constant. The timing spectrum from a synthetic crystal at 25°C is fit by three components: 22% at 2.0 ns, 69% at 15 ns, and 9% at 92 ns, suggesting that the slower components seen in natural crystals are due to impurities not present in synthetic crystals.

1. INTRODUCTION

Although many scintillators have been developed for gamma ray detection, no single scintillator has the combined stopping power of BGO, the luminosity of NaI(Tl) , and the speed of BaF_2 . The recently discovered scintillator lead carbonate (PbCO_3) combines fast decay time, a stopping power similar to that of BGO, but a low light output [1,2]. These properties make lead carbonate

a promising candidate for a high-density high-rate gamma-ray radiation detector. The original work has been extended by measuring the scintillation properties of PbCO_3 as a function of radiation dose, temperature, and chemical purity.

1.1 Previous Measurements on PbCO_3

Although scintillation in cerussite, a naturally occurring mineral form of lead carbonate, was first observed in 1948 [3], its scintillation properties were not quantified until recently [1,4]. The material properties of PbCO_3 are attractive for use as a gamma-ray radiation detector, as its density is 6.6 g/cm^3 , its attenuation length is 1.1 cm for 511 keV photons, and it is not hygroscopic. It is colorless, transmits light down to 270 nm, and is birefringent with indices of refraction of 1.804, 2.077 and 2.079 [5]. This birefringence is an asset, as PbCO_3 scintillation crystals can be oriented so that Fresnel reflection losses at the photomultiplier tube are minimized and that total internal reflection on the other faces is maximized.

The emission spectrum has peaks at 432 and 463 nm, and the emission drops to less than 10% of its peak value at 370 nm and 580 nm. The fluorescence decay lifetime at $+23^\circ\text{C}$, measured with the delayed coincidence method [6], is described by a sum of three exponentials; 24% of the light is emitted with a 5.6 ns time constant, 48% with a 27 ns time constant, and 28% with a 155 ns time constant. Optical quality synthetic crystals of pure lead carbonate have not been available until recently. When a 3 mm cube of a cerussite was excited with 511 keV photons, a photopeak with a 42% full width at half maximum was observed at approximately 9% the light output of a BGO crystal with similar geometry.

2. RADIATION HARDNESS

It is desirable that a scintillator not deteriorate when exposed to high radiation doses. The gamma irradiation facility at Brookhaven National Laboratory [7] was used to determine the effect of radiation on the scintillation properties of PbCO_3 . This facility uses ^{60}Co gamma rays to both induce radiation damage and excite luminescence in scintillators, and has the capability of measuring continuously the total light output and the emission spectrum during irradiation.

A natural crystal of cerussite from Tsumeb, South Africa measuring 8 mm x 8 mm x 4 mm was irradiated at

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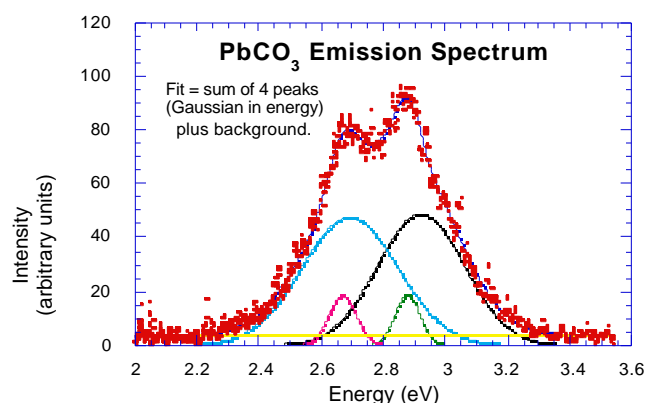


Figure 1: PbCO_3 emission spectrum measured during irradiation superimposed on a constant background.

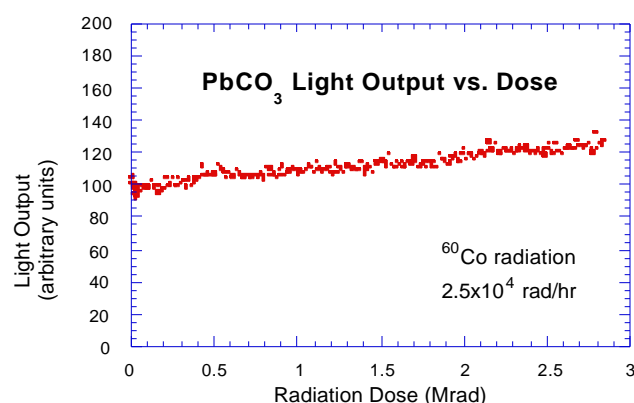


Figure 2: Lead carbonate light output vs. ^{60}Co radiation dose.

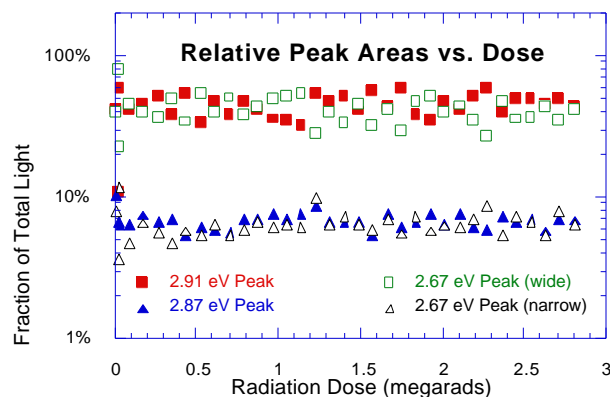


Figure 3: PbCO_3 emission spectrum relative peak intensities vs. ^{60}Co radiation dose.

the BNL facility with ^{60}Co gamma rays at a rate of 2.5×10^4 rad per hour for a period of 120 hours. Although PbCO_3 is optically anisotropic and orientation dependent effects might be present, no attempt was made to orient the crystal or search for anisotropic emission. However the crystal remained in the same position and orientation throughout the series of measurements.

2.1 Light Output vs. Radiation Dose

Both the total light output and emission spectra were measured during irradiation with a scanning monochromator equipped with a cooled, broad spectral response photomultiplier tube. Spectra were recorded every 30 minutes except during the initial part of the irradiation when they were recorded at shorter intervals. Each spectrum was acquired with a sufficient number of one second scans to achieve, by signal averaging, a previously chosen level of precision. These spectra were not corrected for the wavelength dependence of the photomultiplier tube or monochromator.

A typical emission spectrum is shown in Figure 1. The measured spectrum has prominent peaks at 2.87 and 2.67 eV and smaller peaks at approximately 3.00 and 2.55 eV. A sum of 4 Gaussian shaped emission bands plus a flat background is required to adequately describe the emission spectrum, as fewer bands result in an unacceptable fit. The resulting fit along with its individual components is also shown in Figure 1. Each of the spectra acquired during irradiation was fitted to the function described above, where all of the fit parameters (the peak energy, width, and area of all four Gaussians plus the background level) were allowed to vary.

Figure 2 shows the total light output (the sum of the four fit emission peak areas) as a function of radiation dose. The output increases roughly linearly with radiation dose at 9% per Mrad of ^{60}Co irradiation. Quantitative radiation damage measurement ended at a total dose of 3 Mrad, but the sample was exposed to 10 Mrad without any visible coloration. While it is unusual for luminescence to increase with radiation dose, this effect has been observed before in BC-408 and BC-412 plastic scintillator [8,9]. Four examples of luminescence mechanisms that could lead to increasing light output with radiation dose are: 1) the unirradiated crystals contain absorption bands that are removed by radiation, 2) the luminescence is due to lattice defects produced by radiation, 3) the luminescence is due to a charge transfer process that is in competition with recombination at traps, and radiation reduces the recombination probability at the traps, 4) the luminescence is due to a lattice defect or impurity that is "poisoned" by near atoms or defects, and the radiation causes the poisoning atom or defect to diffuse away from the emission center.

2.2 Emission Spectrum vs. Radiation Dose

The scintillation emission spectrum was measured during irradiation and fitted using the technique described above. The central energy and width of each of the four peaks remained constant, within the errors of the fit, as a function of radiation dosage. The values for the peak energy and FWHM are 2.91 eV (0.33 eV), 2.87 eV (0.11 eV), 2.67 eV (0.33 eV), and 2.67 eV (0.11 eV).

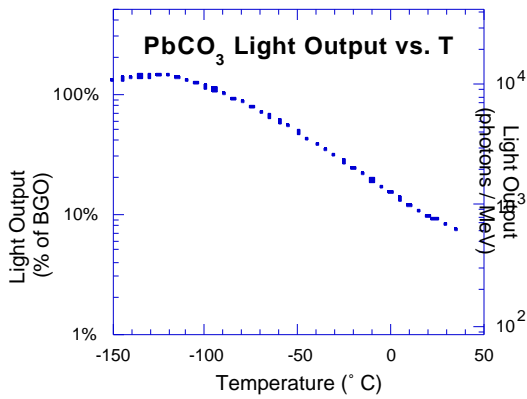


Figure 4 Lead carbonate light output vs. temperature.

The fraction of light in each of the four peaks (that is, the fit area of each peak divided by the total light output) also remained constant during irradiation, as shown in Figure 3. Thus, while the total light output increased by over 25% during the course of the nearly 3 Mrad irradiation, the emission spectrum remained constant.

3. TEMPERATURE DEPENDENCE

It was noted in earlier papers [1,4] that the PbCO_3 scintillation light output depended strongly on temperature. While explicit decay time measurements were not made, observations of oscilloscope traces indicated that the fast decay time component did not change as the temperature was reduced, but a long (1 μs) component appeared [1]. Since it is likely that the optimal operating temperature for lead carbonate is below room temperature, a more accurate measurement of the light output and the decay time distribution as a function of temperature have been made as a function of temperature.

3.1 Light Output vs. Temperature

Since the decay time of PbCO_3 is temperature dependent, it is necessary to measure the total light output in a way that is insensitive to changes in the scintillation decay time. This was done by exciting a PbCO_3 sample with a 2 mCi ^{68}Ge source and counting the single photon rate with a cooled photomultiplier tube placed 25 cm away from the scintillator.

The sample was contained in a thermally insulated, temperature controlled housing with the source placed next to the crystal. A 2 inch diameter Hamamatsu R-2059 photomultiplier tube was located in a separate, thermally insulated, temperature controlled housing and cooled to -20°C to reduce the single photon dark count rate to less than 1% of the PbCO_3 signal at $+23^\circ\text{C}$. A double wall, vacuum insulated fused silica window allowed the scintillation light to pass from the scintillator to the photomultiplier tube while maintaining separate temperature environments. A two inch thick block of lead placed between the source and the photomultiplier

tube prevented direct interactions in the photomultiplier tube. The output of the photomultiplier tube was converted to a logic pulse with a constant fraction discriminator and counted with a CAMAC scaler.

The resulting count rate is shown, as a function of temperature, in Figure 4 after converting to absolute light output by using the previously measured light output of 620 photons per MeV at 23°C . The light output increases at a roughly exponential rate with decreasing temperature until it reaches a maximum value at -125°C , at which point the light output begins to decrease slightly.

3.2 Decay Time vs. Temperature

The fluorescent decay lifetime was measured using the delayed-coincidence method of Bollinger and Thomas [6], as modified by Moszynski and Bengtson [10]. A piece of barium fluoride scintillator coupled to a Hamamatsu R-2059 photomultiplier tube provided a start signal, and another quartz-windowed Hamamatsu R-2059 photomultiplier tube placed 25 cm away from the PbCO_3 sample provided the stop signal. As with the total light output measurement, the PbCO_3 sample was in a thermally insulated, temperature controlled housing and the single photon photomultiplier tube was cooled to -20°C to reduce dark current. A 10 μCi ^{22}Na source provided the 511 keV photon pairs that excited both the BaF_2 scintillator and the PbCO_3 scintillator sample. Timing signals from both photomultiplier tubes were generated using a constant fraction discriminator, and the time difference between the start and stop signals was digitized with a time to amplitude converter and an analog to digital converter.

The decay time of the components extend from 1 ns to above 3 μs . Therefore two timing data sets were collected at each temperature, one with fine timing resolution (0.3 ns/bin) that covered a small dynamic range (600 ns) and one with coarse time resolution (3.0 ns/bin) that covered a larger dynamic range (6 μs). These two data sets were simultaneously fit with a sum of four exponential decay lifetimes plus a constant background. Two typical timing distributions, with the data binned into coarser bins for clarity, are shown in Figure 5.

A pair of decay time data sets were collected at a variety of temperatures ranging from -140°C to $+30^\circ\text{C}$, and each pair simultaneously fit with the 4 component fit described above. The variation of the 4 decay lifetimes with temperature is plotted in Figure 6. While correlations make it difficult to accurately measure individual lifetimes, the overall tendency is for the lifetimes to increase with decreasing temperature. A notable exception is τ_1 (the fastest component), which increases until approximately -50°C and then abruptly decreases. Note that Component 4, the long ($>1 \mu\text{s}$) component that was previously seen only at low temperatures, is actually present in small amounts at all temperatures.

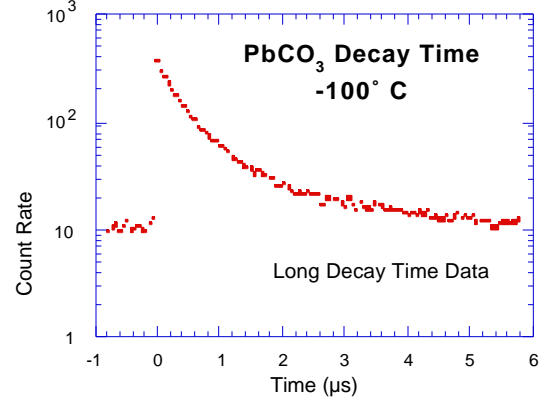
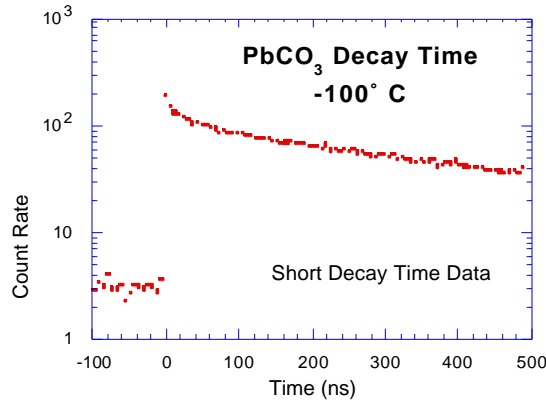


Figure 5: Lead carbonate decay time distribution at -100°C . Data on the left was taken with 0.3 ns bins, data at the right was taken with 3 ns bins. For clarity, only one twentieth of the data points are displayed.

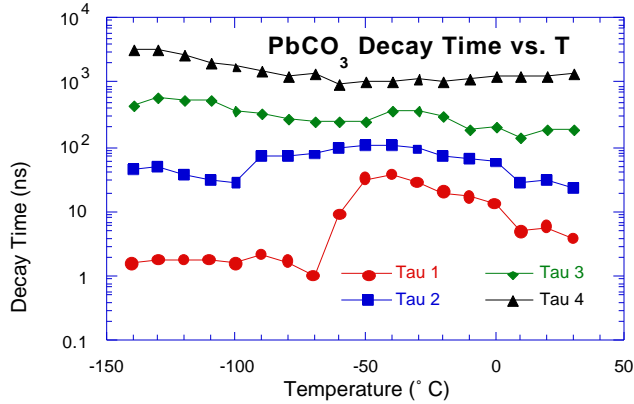


Figure 6: PbCO_3 decay component lifetimes vs. temperature.

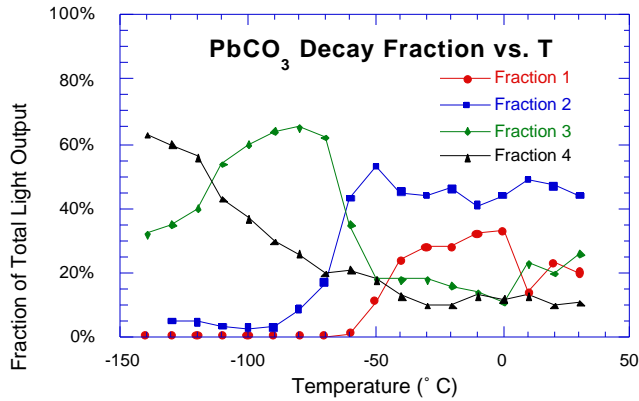


Figure 7: PbCO_3 decay component fractions vs. temperature.

The relative intensities of each component also vary greatly as a function of temperature, and are plotted in Figure 7. Again, significant correlations between the components are present, but are smaller than the correlations between decay lifetimes. The overall trend is that the majority of the light is contained in the two fastest components for temperatures above -50°C , and the two slower components dominate below -50°C .

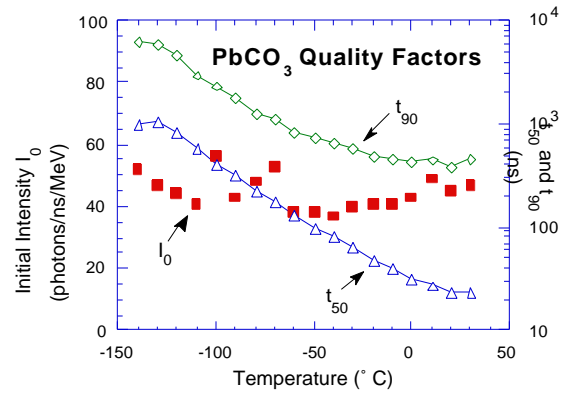


Figure 8: Lead carbonate initial intensity I_0 and times t_{50} and t_{90} vs. temperature. See text for definitions.

It is difficult to determine the optimal operating temperature from the light output and decay lifetime values described above. Therefore we have computed, based on the fit parameters, several measures of the decay time distribution that describe the spectrum in terms that are useful when using scintillators as radiation detectors. First, we compute the initial intensity I_0 , which has units of number of photons per ns per MeV of incident energy. This number aids in estimating the attainable timing resolution of the scintillator. We also compute t_{50} and t_{90} , which are the times that it takes to emit 50% and 90% of the total number of photons. The t_{50} value helps estimate the amplifier shaping time, while t_{90} is useful in estimating the dead time of the scintillator. These values are plotted as a function of temperature for lead carbonate in Figure 8. For comparison, the values for I_0 , t_{50} , and t_{90} for BGO at 25°C are 39 photons per ns per MeV, 160 ns and 590 ns respectively.

Figure 8 shows that the initial intensity I_0 is approximately 45 photons/ns/MeV independent of temperature, while t_{50} (t_{90}) increases from 25 ns (500 ns) to 1 μs (6 μs) with decreasing temperature. Thus, while the overall increase in the decay time with decreasing temperature increases the amplifier shaping time and dead time of a

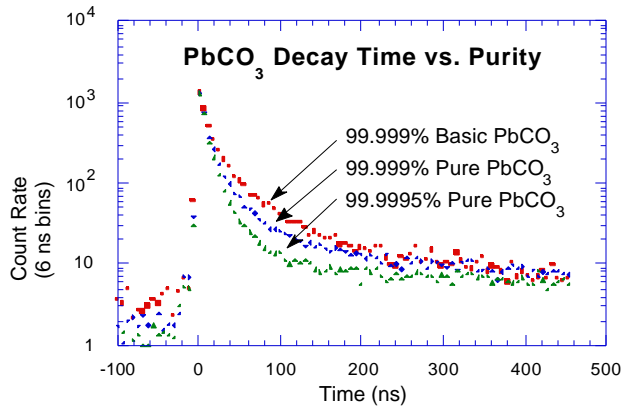


Figure 9 Lead carbonate decay time distribution vs. purity.

Table 1: Decay time fit and light output of powdered sample of lead carbonate.

	99.999% Basic PbCO ₃	99.999% Pure PbCO ₃	99.9995% Pure PbCO ₃
Component 1	26% @ 5.1 ns	19% @ 2.7 ns	22% @ 2.7 ns
Component 2	47% @ 25 ns	42% @ 16 ns	41% @ 12 ns
Component 3	23% @ 118 ns	17% @ 105 ns	10% @ 47 ns
Component 4	4% @ 1.2 μ s	22% @ 1.2 μ s	27% @ 1.2 μ s
Light Output (% of BGO)	8.0%	4.1%	3.5%

system using PbCO₃, the increasing light output maintains a constant initial photon rate and so the timing resolution will not deteriorate with decreasing temperature.

4. PURITY DEPENDENCE

Until recently it has been impossible to obtain synthetic optical quality crystals of lead carbonate. Consequently, the first scintillation lifetime measurements were made with a powdered sample of basic lead carbonate 2(PbCO₃)·Pb(OH)₂ excited with 22.7 keV x-rays [11] and subsequent measurements were made with an optical quality cerussite crystal [1]. As a result, there has been some speculation that the fluorescence properties are not intrinsic, but are the result of an impurity. To address these concerns we repeated the x-ray stimulated measurements with powdered samples of high purity lead carbonate and measured the scintillation properties of synthetic PbCO₃ crystals.

4.1 X-Ray Measurements of High Purity Powders

An accurate measurement of the fluorescence decay time and an estimate of the total light output of a scintillator can be made by exciting a powdered sample of the scintillator with a nanosecond wide burst of x-rays from a synchrotron light source, then observing the emitted light with a photomultiplier tube [11]. The decay time spectrum of each sample is obtained using the delayed coincidence method [6] where a signal synchronized with the x-ray arrival time was generated with a plastic

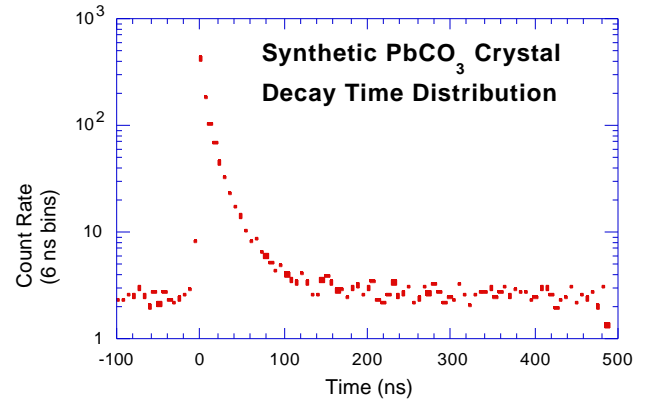


Figure 10 Decay time distribution of synthetic PbCO₃.

scintillator and a photomultiplier tube [12]. Measurements were made on powdered samples of lead carbonate having different purity and chemical form, namely 99.999% basic lead carbonate 2(PbCO₃)·Pb(OH)₂, 99.999% lead carbonate PbCO₃, and 99.9995% lead carbonate PbCO₃. Note that the first sample (99.999% basic lead carbonate) was the chemical used in reference [11].

The decay time spectra, shown in Figure 9, are normalized so that the initial counting rate is the same for all three samples. Figure 9 shows that while the overall shape of the curves are similar, the magnitude of the slower components decrease with increasing purity. This change has been quantified by fitting the curves to the sum of four exponential decay components, with the time constant of one component fixed at 1.2 μ s, plus a constant background. The results are given in Table 1.

Increasing the purity tends to affect the slower components the most, halving both the decay time and fraction of the third component but increasing the fraction of the fourth component. The two fastest components are relatively constant, and so the net effect is to decrease the total light output by removing some of the slow light. This suggests that while the fast light is intrinsic, some of the slow light may be due to impurities.

4.2 Measurements on Synthetic Crystals

The usefulness of lead carbonate as a radiation detector has been limited because it has, until recently, been impossible to grow optical quality synthetic crystals. However Sawyer Research Products, Inc. of Eastlake, OH has recently grown some small (3 mm typical dimension) synthetic crystals of PbCO₃. These crystals are quite clear, but have several internal fractures that made uniform light collection impossible. Thus we were unable to detect a 511 keV photopeak, but were able to determine that the scintillation light output was similar in magnitude to a cerussite crystal of similar quality.

The synthetic crystals were luminous enough to measure their decay time distribution at room temperature. The decay time distribution, shown in Figure 10, is fitted

by the sum of 3 exponential terms (22% @ 2.0 ns, 69% @ 15 ns, and 9% @ 92 ns) plus a constant background. The signal to noise ratio is not sufficient to measure the fourth (typically 1.2 μ s) component. These values, while consistent with the cerussite values, are in best agreement with the fit to the high purity (99.9995%) PbCO_3 powder. Again, this suggests that a portion of the slower components may be due to impurities.

5. CONCLUSIONS

The scintillator PbCO_3 is quite resistant to radiation damage. It exhibited a 25% increase in luminescence and no change in the emission spectrum after 3 Mrad of ^{60}Co irradiation. During 10 Mrad of irradiation the crystal showed no signs of coloring. The light output and emission time spectrum depend strongly on temperature. The light output increases by a factor of almost 20 as the temperature is reduced from +30° C to the peak emission temperature of -125° C. The decay time tends to increase as the temperature is lowered, but does so in a way such that the initial number of photons per ns is temperature independent. Higher purity powdered samples have a lower light output than less pure samples but the decay times are longer. Finally, scintillation from synthetic crystals has been observed, and, while the optical clarity was not sufficient to observe a 511 keV photo-peak, the decay time spectrum at room temperature agrees with the cerussite decay time spectrum.

Further work remains to be performed before lead carbonate can be used as a practical radiation detector. The greatest challenge is to produce large volume, optical quality crystals, and while this promises to be difficult, encouraging progress has been made in the last year. In addition, further radiation damage studies must be made on PbCO_3 at a facility capable of simultaneously measuring the luminescence and absorption properties.

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Reference to a company or product name does not imply approval or recommendation by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

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